Diastereoselective Insertion of Isocyanide into the Alkyl−Metal Bond of Methylbenz[*e*]indenyl *ansa*-Zirconocene Complexes

Alfredo Sebastián,[a] Pascual Royo,*[a] Pilar Gómez-Sal,[a] and Carmen Ramírez de Arellano[b]

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Alkylation of *ansa*-zirconocene [Zr{(η^5-C_5H_5)$SiMe_2$-(MBI)}Cl_2] (MBI = η^5-2-Me–$C_{13}H_7$) with MgRCl gave the dimethyl complex [Zr{(η^5-C_5H_5)$SiMe_2$(MBI)}Me_2], but unresolvable mixtures containing mono-alkylated compounds were obtained when bulkier alkyls were used. However pure dialkyl complexes [Zr{(η^5-C_5H_5)$SiMe_2$(MBI)}R_2] (R = CH_2Ph, CH_2SiMe_3) were easily obtained using K(CH_2Ph) and Li(CH_2SiMe_3) as alkylating agents. Diastereoselective insertion into the MBI-unprotected Zr–R bond was observed when all of these dialkyl complexes were treated with 2,6-xylyl isocyanide to give the iminoacyl compounds [Zr{(η^5-C_5H_5)$SiMe_2$(MBI)}R{CR[η^2-*N*-(2,6-xylyl)]}] (R = Me, CH_2Ph, CH_2SiMe_3). All of the new complexes were characterized by NMR spectroscopy and the X-ray molecular structures of the dibenzyl and the imino-benzyl compounds were determined. The catalytic activity for ethene polymerization and ethene/1-hexene copolymerization of the dichloro zirconocenes [Zr{(η^5-C_5H_5)EMe_2(MBI)}Cl_2] (E = C, Si), activated with methylalumoxane (MAO), was measured.

Introduction

The rational design of different types of group 4 metallocenes to be used as olefin polymerization catalysts, after activation with methylalumoxane (MAO), has been the objective of a great number of scientific contributions.[1−5] Extensive studies have demonstrated the high degree of electronic and steric control provided by sterically demanding cyclopentadienyl ligands, making them powerful tools for producing convenient single-site catalysts for the known broad range of precisely functionalized, tacticity-controlled, branched and block polymers and copolymers.[6−8] The main targets of many of the studies have been the optimization of catalytic activity, stereospecificity and the modulation of the molecular weight of the resulting polymers.[9,10] It is well-known that the presence of condensed benzene rings in the indenyl ligands of metallocene-type complexes induces a remarkable increase in their catalytic activity, and the addition of a 2-methyl substituent in their Cp rings reduces the incidence of β-elimination processes, providing a significant increase in the molecular weight of the polymer. In this regard the 2-methylbenz[*e*]indenyl ligand (MBI) is an excellent choice for this purpose. The isolation of the first group 4 metallocenes containing this ligand has demonstrated high performance in ethylene and propylene polymerization[11,12] as well as in copolymerization processes using ethylene and octene[13] or ethylene/polar monomers such as 10-undecene-1-ol and allyl alcohol.[14,15]

Metal alkyl compounds are convenient models not only for olefin polymerization but also for other insertion and transmetallation reactions and as carbon−carbon bond formation precursors.[16−18] Insertion of unsaturated substrates into metal−alkyl bonds are basic reactions for which many synthetic, mechanistic and theoretical studies have been developed.[19] The migratory insertion of isocyanide has provided numerous iminoacyl complexes[20−24] and a solid knowledge of the steric and electronic effects of the ligands on the reactivity[25] and catalytic activity[9] of different systems.

We report herein the effect of the bulky MBI ligand on the stereoselectivity of the migratory insertion of 2,6-dimethylphenyl isocyanide into the metal−alkyl bonds of new dialkyl metallocenes prepared from the dichloro derivatives reported recently.[26] We also report the results found from our studies of catalytic activity of these dichloro-metallocenes in the homopolymerization of ethylene and copolymerization of ethylene/1-hexene.

Results and Discussion

The dichloro *ansa*-zirconocenes [Zr{(η^5-C_5H_5)EMe_2(η^5-2-Me−$C_{13}H_7$)}Me_2] (E = C: **1a**, E = Si: **1b**) containing the

[a] Departamento de Química Inorgánica, Universidad de Alcalá
Campus Universitario, 28871 Alcalá de Henares, Spain
Fax: (internat.) + 34-91-8854683
E-mail: pascual.royo@uah.es
[b] Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia
46100 Valencia, Spain

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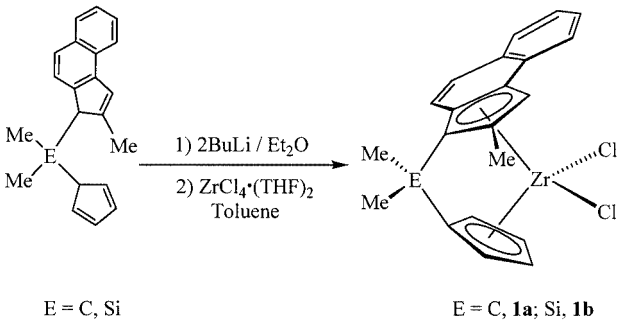
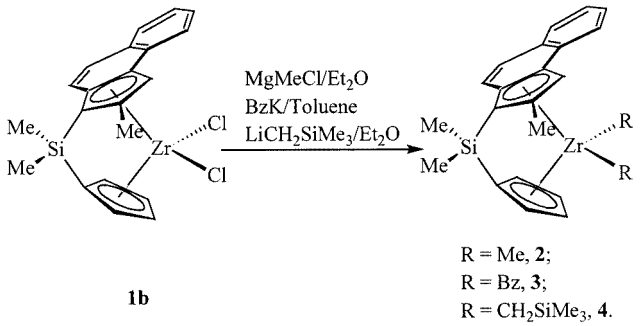
MBI ligand were isolated previously[26] by reaction in toluene of $ZrCl_4(THF)_2$ with the dilithium salts of the corresponding $-CMe_2-$ and $-SiMe_2$-bridged indenyl-cyclopentadienyl derivatives, as shown in Scheme 1.



Scheme 1

The reaction of complex **1b** with 2 equiv. of MgClMe gave dimethyl zirconocene [Zr{(η^5-C_5H_5)$SiMe_2$(η^5-2-Me$-C_{13}H_7$)}Me_2] (**2**) in high yield. However this type of dialkyl compound is not so easily accessible when bulky substituents are located at the cyclopentadienyl β-carbon of rigid *ansa*-metallocenes. The steric demands of the benzene rings attached to the α and β positions of the η^5-cyclopentadienyl unit in the MBI ligand of complex **1b**, make dialkylation difficult when bulky alkyl groups are used. In fact alkylation of **1b** with two equiv. of $MgCl(CH_2Ph)$ gave low yields of the dibenzyl complex [Zr{(η^5-C_5H_5)$SiMe_2$(η^5-2-Me$-C_{13}H_7$)}$(CH_2Ph)_2$] (**3**) which was always contaminated by significant amounts of the monobenzyl compounds. However complex **3** could be isolated in high yield as the unique component when $K(CH_2Ph)$ was used as the alkylating agent. Similarly, $MgCl(CH_2SiMe_3)$ has been extensively used[27,28] to produce dialkyl derivatives of many metallocenes with free cyclopentadienyl ligands, whereas related *ansa*-metallocenes usually yield the corresponding monoalkyl compounds.[29] Consistently the dialkyl complex [Zr{(η^5-C_5H_5)$SiMe_2$(η^5-2-Me$-C_{13}H_7$)}$(CH_2SiMe_3)_2$] (**4**) could not be isolated using the Grignard reagent but was easily obtained in high yield with the lithium derivative $Li(CH_2SiMe_3)$. It is therefore evident that the steric hindrance due to the bulky MBI ligand may be overcome using more appropriate nucleophilic alkylating agents, as shown in Scheme 2. The air sensitive dialkyl compounds **2**–**4** are



Scheme 2

stable in $CDCl_3$ under an inert atmosphere although they are transformed into the dichloro complex **1b** when heated at 110 °C in Teflon-valved NMR tubes.

The enantiotopic face of the MBI ligand makes these dialkyl compounds, **2**–**4,** asymmetric molecules with two nonequivalent alkyl groups. The ^{1}H NMR spectrum of **2** shows two singlets for the Zr-methyl groups, one shifted significantly highfield ($\delta = -1.29$) compared with the typical value ($\delta = 0.09$ ppm) observed for the other, which was in the range found for related methyl zirconocenes.[30] NOE experiments demonstrated that the highfield singlet is due to the methyl group located under the benzene ring attached to the indenyl moiety. Similar behavior was observed for the four doublets due to the two diastereotopic methylene protons of the benzyl (**3**) and methylsilyl (**4**) ligands. Two of the signals, corresponding to the alkyl group located under the ring-fused benzene, are shifted highfield ($\delta = 0.18$ ppm and 0.28 ppm for **3**; $\delta = -2.20$ ppm and -0.94 ppm for **4**) due to the anisotropic effect of the aromatic ring. However this anisotropic contribution was not observed in the ^{13}C and gHMQC NMR spectra (see Exp. Sect.). In addition, the ^{1}H NMR spectra of complexes **2**–**4** show the expected singlet for the MBI-methyl group, two singlets for Si–Me, four multiplets for the C_5H_4 ring and one singlet for the C_5H(MBI) ring proton. All of the remaining MBI nonequivalent protons give the set of signals corresponding to two AB and ABCD spin systems.

Slow cooling at −30 °C of a toluene solution of the dibenzyl complex **3** rendered appropriate crystals for X-ray diffraction studies. The X-ray structure of **3** is shown in Figure 1 with the atomic labeling scheme and selected bond lengths and angles are listed in Table 1.

The coordination geometry of the zirconium atom is the typical distorted tetrahedron formed by the two ring centro-

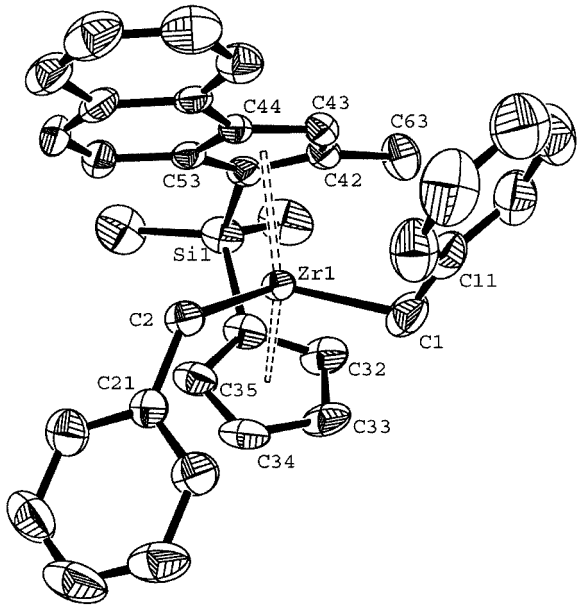
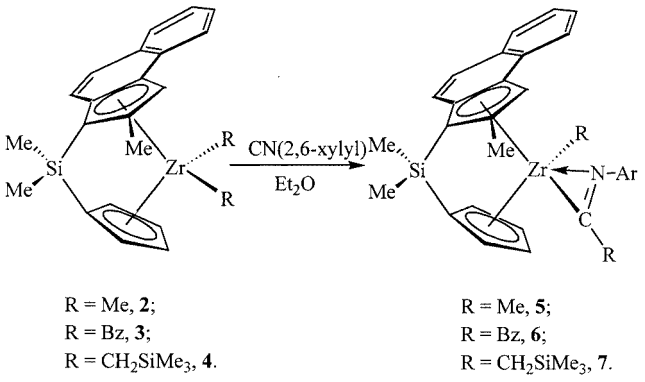


Figure 1. Ellipsoid plot of compound **3** (50% probability level); hydrogen atoms have been omitted for clarity

Table 1. Selected interatomic distances (Å) and angles (°) for complex **3** (Cp is the centroid of C(31)−C(32)−C(33)−C(34)−C(35) ring; Cp_{MBI} is the centroid of C(41)−C(42)−C(43)−C(44)−C(45) ring)

Zr(1)−Cp	2.212	Zr(1)−C(33)	2.556(4)
Zr(1)-Cp_{MBI}	2.262	Zr(1)−C(34)	2.559(5)
Zr(1)−C(2)	2.308(4)	Zr(1)−C(35)	2.491(5)
Zr(1)−C(1)	2.315(6)	Zr(1)−C(41)	2.515(4)
C(1)−C(11)	1.478(8)	Zr(1)−C(42)	2.514(4)
C(2)−C(21)	1.481(6)	Zr(1)−C(43)	2.578(4)
Zr(1)−C(31)	2.491(5)	Zr(1)−C(44)	2.636(4)
Zr(1)−C(32)	2.487(5)	Zr(1)−C(53)	2.582(4)
C(2)−Zr(1)−C(1)	97.4(2)	C(11)−C(1)−Zr(1)	121.8(4)
Cp−Zr(1)−Cp_{MBI}	125.8	C(21)−C(2)−Zr(1)	125.5(3)



Scheme 3

ids and the carbon atoms of the benzyl ligands. The Cp(centroid)−Zr−Cp_{MBI}(centroid) [125.8°] and the C(2)−Zr(1)−C(1) [97.4(2)°] angles are similar to those observed for related *ansa*-MBI compounds and the Cp(centroid)−Zr distances [Cp 2.212Å and Cp_{MBI} 2.262Å] are in the range found in related indenyl zirconocenes.[12,26,31,32]

The most remarkable difference is the orientation of the two nonequivalent benzyl ligands. One is located above the plane (torsion angle Cp_{MBI}−Zr(1)−C(1)−C(11) 62.6°) while the other is located below (torsion angle Cp_{MBI}−Zr(1)−C(2)−C(21) 158.1°), with respect to the C(1)−Zr(1)−C(2) plane. The benzyl ligand eclipsed by the MBI system positions the methylene C(2) under the benzene ring condensed to the indenyl moiety with the phenyl ring oriented towards the other Cp system, whereas the benzyl ring located on the open side, far away from the MBI system, has its phenyl ring directed towards the moiety with the MBI system using the wide space. In spite of these different orientations both benzyl ligands show Zr−C distances [Zr−C(1) 2.315(6) Å and Zr−C(2) 2.308(4) Å] and Zr−C−C(Ph) angles [Zr−C(1)−C(11) 121.8(4)° and Zr−C(2)−C(21) 125.5(3)°] typical of σ-bonded benzyl groups without benzallylic interactions [Zr−C(11) 3.338 and Zr−C(21) 3.389 Å], and are similar to values found[31,33] for other benzyl zirconium compounds with bulky Cp systems.

Reaction of diethyl ether solutions of the dialkyl complexes **2**−**4** with 1 equiv. of 2,6-xylyl isocyanide at room temperature gave the corresponding iminoacyl compounds [Zr{(η^5-C_5H_5)$SiMe_2$(η^5-2-Me−$C_{13}H_7$)}R{CR[η^2-*N*-(2,6-xylyl)]}] (R = Me: **5**, CH_2Ph: **6**, CH_2SiMe_3: **7**) as shown in Scheme 3, which were isolated as solids and characterized by elemental analysis and NMR spectroscopy. When monitoring the reactions by ^1H NMR spectroscopy it was observed that insertion was easier for less bulky alkyl ligands following the order **5** < **6** < **7**. The η^2-coordination of the isocyanide ligand is consistent with the IR [(Nujol): $\tilde{\nu}_{C=N}$ = 1600, 1585 and 1590 cm^{-1}] and ^{13}C NMR spectroscopic data [δ = 245.4 (**4**), 244.5 (**5**), 245.4 (**6**)]. Further reactions with an additional 1 equiv. or an excess of isocyanide were not observed under any conditions, as was expected for these types of coordinately saturated 18e species.

These insertion reactions may lead to two diastereomers depending on which of the two nonequivalent alkyl groups migrate to the isocyanide ligand. The ^1H NMR spectra confirm that one unique diastereoisomer is obtained in all of these reactions, for which the signals due to the alkyl group located under the MBI system remain almost unmodified [δ = −1.20(s) (**5**), 0.27(d) and 0.56(d) (**6**), −1.86(d) and −2.97(d) (**7**)]. In contrast, signals due to the alkyl group located far from the MBI system are significantly shifted lowfield [δ = 2.36(s) (**5**), δ 3.60(d) and 3.68(d) (**6**), 2.45(d) and 2.63(d) (**7**)] as expected for the migrated C-bonded alkyl ligand. NOE experiments on the methyl derivative (**5**) demonstrate that the highfield shifted singlet corresponds to the methyl group located under the MBI system, which is affected by the anisotropic effect of the aromatic ring.

Similar behavior is also observed in the ^{13}C NMR spectra which show significant lowfield shifts for all the signals due to the migrated alkyl group bound to the iminoacylic carbon atom, appearing at δ = 22.2, 44.6 and 22.7 for **5**, **6** and **7**, respectively. All of the remaining ^1H and ^{13}C NMR signals show no significant changes.

The ^1H NMR spectrum of complex **7** represented in Figure 2 shows the typical pattern of signals observed for both dialkyl and iminoacyl complexes.

Therefore it is possible to conclude that the steric demands of the bulky MBI system have a significant effect on the high diastereoselectivity of all of these insertion reactions, although the electronic contribution demonstrated for related [MBI]-silyl-η^1-amido zirconium complexes (work still in progress),[34] for which electronic effects are significantly important, cannot be discarded. However the spectroscopic data do not distinguish between the *exo*-*N*-coordinated iminoacyl formed under kinetic control and the usually more favorable *endo*-*N*-coordinated iminoacyl isomer formed under thermodynamic control. The *endo*-configuration was confirmed for complex **6** by X-ray diffraction studies of its molecular structure.

Appropriate crystals of **6** were isolated by slow evaporation of a C_6D_6 solution. Figure 3 shows the X-ray molecular structure of **6** with the atomic labeling scheme. Selected bond lengths and angles are collected in Table 2.

The pseudotetrahedral coordination of the zirconium atom is defined by the Cp, the Cp_{MBI}, the benzyl methylene

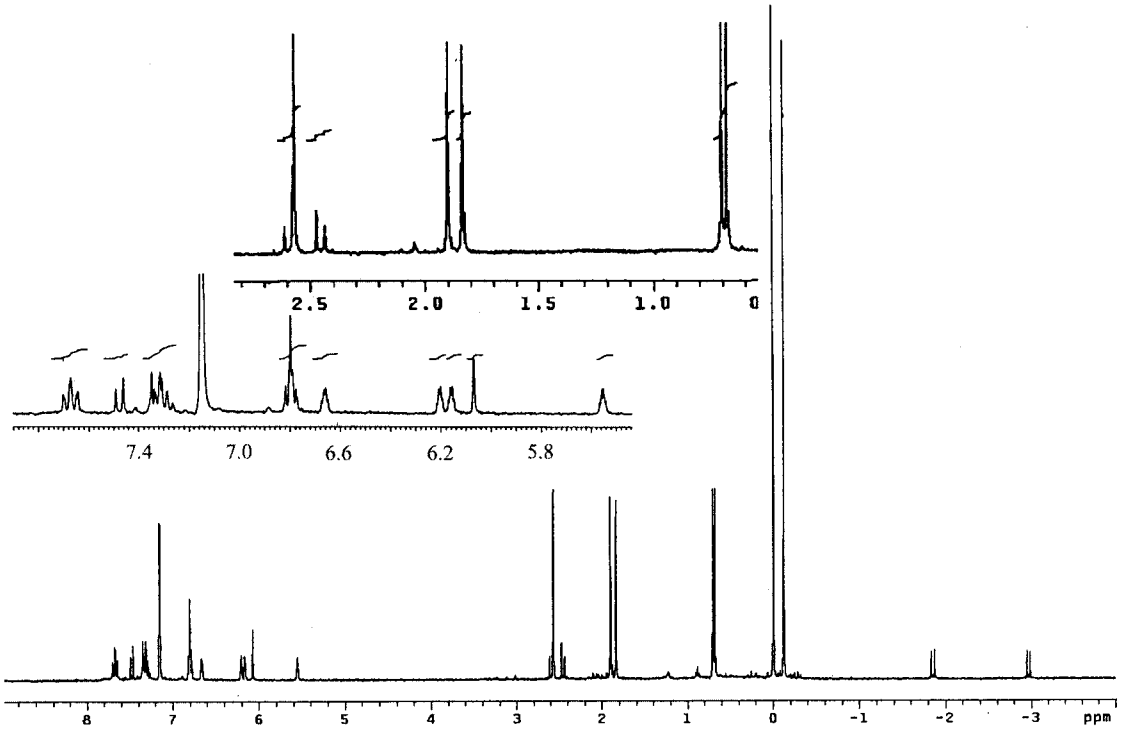


Figure 2. ^{1}H NMR for **7** in C_6D_6; the spectrum shows the normal pattern of signals for Zr(MBI−$SiMe_2$Cp)R_2 complexes

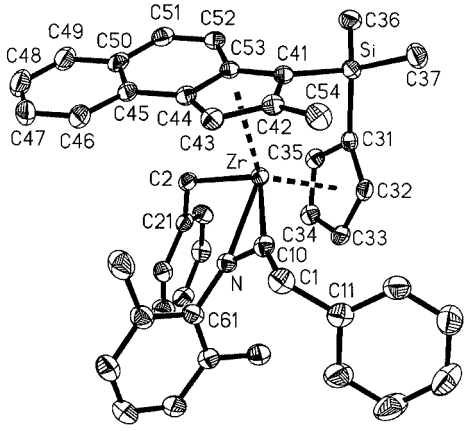


Figure 3. Ellipsoid plot of compound **6** (50% probability level); hydrogen atoms have been omitted for clarity

Table 2. Selected interatomic distances (Å) and angles (°) for complex **6**
Cp is the centroid of C(31)−C(32)−C(33)−C(34)−C(35) ring. Cp_{MBI} is the centroid of C(41)−C(42)−C(43)−C(44)−C(45) ring.

Zr−Cp_{MBI}	2.311	Zr−C(32)	2.547(2)
Zr−Cp	2.246	Zr−C(33)	2.605(2)
Zr−N	2.287(2)	Zr−C(34)	2.564(2)
Zr−C(10)	2.231(2)	Zr−C(35)	2.492(2)
Zr−C(2)	2.372(2)	Zr−C(41)	2.548(2)
C(1)−C(10)	1.513(3)	Zr−C(42)	2.530(2)
C(2)−C(21)	1.468(3)	Zr−C(43)	2.607(2)
N−C(10)	1.281(3)	Zr−C(44)	2.708(2)
Zr−C(31)	2.532(2)	Zr−C(53)	2.649(2)
Cp_{MBI}−Zr−Cp	124.3	C(21)−C(2)−Zr	123.24(13)
C(10)−Zr−N	32.92(6)	C(10)−N−Zr	71.12(12)
C(10)−Zr−C(2)	116.43(7)	C(61)−N−Zr	161.83(13)
N−Zr−C(2)	84.18(6)	N−C(10)−C(1)	124.31(19)
C(1)−C(10)−Zr	159.54(15)	N−C(10)−Zr	75.96(12)

carbon and the midpoint of the iminoacyl C−N bond. Both, the Cp−Zr and Cp_{MBI}−Zr lines are almost perpendicular to the corresponding C(31)−C(35) and C(41)−C(53) cyclopentadienyl main planes (87.3 and 85.0°, respectively). The Cp−Zr−Cp_{MBI} bond angle [124.3°] is closer than that observed for complex **3** indicating the larger bite of the cyclopentadienyl rings. The structure shows η^2-coordination of the iminoacyl ligand with the C−N bond almost perpendicular to the line going from the Zr atom to the C−N bond midpoint (87.4°). The iminoacylic-N adopts an *endo*-configuration, with a C(2)−Zr−C(10)−N torsion angle of 12.6(1)°, giving rise to a very open C(2)−Zr−C(10) angle [116.44(7)°]. The benzyl ligand is eclipsed by the MBI system, locating the methylene C(2) under the benzene ring condensed to the cyclopentadienyl moiety [C(2)−Zr−C(44)−C(45) torsion angle 16.4(2)°]. The phenyl group of the benzyl ligand [C(21)−C(26)] is *anti* to the MBI system with respect to the Zr−C(2) bond [C(21)−C(2)−Zr−Cp_{MBI} torsion angle 178.0°]. Thus, the benzyl group adopts a geometry similar to that observed for the eclipsed benzyl group in compound **3**.

The zirconium-carbon bond length [Zr−C(2) 2.372(2) Å] to the sp^3 methylene benzyl ligand is 0.06Å longer than that observed in complex **3** and longer than the distance to the sp^2 iminoacyl carbon atom[35] [Zr−C(10) 2.231(2) Å], which is in the range [2.164−2.363Å] observed for related iminoacyl zirconium compounds.[21,36] However the zirconium-nitrogen bond length [Zr−N 2.2872(16) Å] is

slightly longer than those found in related zirconium iminoacyl compounds in the range 2.148−2.250Å.[37,38] The double bond character of the iminoacyl C(10)−N bond is confirmed by the 1.281(3) Å distance, which is longer than usual for related zirconium iminoacyl compounds and close to that known for organic C=N bonds [1.28Å].[35] All of these elongated bonds are consistent with the steric hindrance due to the bulky MBI ring and the benzyl and 2,6-xylyl substituents.

Both the iminoacyl N and the C(10) sp^2 atoms show a profoundly distorted trigonal planar disposition, although the sum of their angles is 360°. The distortion is mainly seen in the close C(10)−N−Zr [71.13(12)°] and N−C(10)−Zr [75.95(12)°] angles and together with the small angle at the zirconium center [C(10)−Zr−N 32.92(6)°] are a consequence of the η^2-coordination of the iminoacyl ligand.

The Zr−Cp distance [2.246Å] is shorter than the $Zr-Cp_{MBI}$ distance [2.311Å]. Consistently the distances from zirconium to the Cp ring carbon atoms [2.492(2)−2.605(2) Å] are slightly shorter than the corresponding distances to the MBI carbon atoms [2.530(2)−2.708(2) Å], the Zr−C(44) and Zr−C(53) bond lengths being unusually long [2.708(2) and 2.649(2) Å, respectively].

Olefin Polymerization Results

The dichlorozirconocenes **1a** and **1b**, activated with a large excess methylalumoxane (MAO), were used as catalyst precursors for the polymerization of ethylene and copolymerization of ethylene/1-hexene. All experiments were carried out at 70 °C in heptane for 15 min, under 4.0 bar of ethylene in a Büchi autoclave, with variable amounts of catalyst and a 10% toluene solution of MAO.

The reaction conditions, measured activities and properties of the resulting polymers are summarized in Table 3 and compared with data for $[ZrCp_2Cl_2]$ and $[Zr(SiMe_2Cp_2)Cl_2]$ used as references.

Both catalysts **1a** and **1b** polymerize ethylene to give linear polyethylene with high activities. Complex **1b** shows a catalytic activity four times higher than that observed for complex **1a** (entries 1, 6) leading to a polymer of much higher molecular weight, similar to that observed for $[ZrCp_2Cl_2]$, although their polydispersities are similar. Under similar conditions (entries 3, 9) complex **1b** is significantly more active than $[ZrCp_2Cl_2]$ and almost 10 times more active than $[Zr(SiMe_2Cp_2)Cl_2]$. Increasing Al/Zr ratios (entries 3, 4 and 5, 6) produce higher activities which were only slightly dependent on the catalyst concentration.

Both metallocenes show higher catalytic activities (entries 1, 2 and 4, 7, 8) in the presence of the comonomer 1-hexene as a consequence of the known "comonomer effect".[39] In all cases incorporation of 1-hexene to the polymer chain is rather high for both catalysts, and is significantly higher (6.69%) for the methylene-bridged complex **1a** with its more open bite compared to the silyl-bridged complex **1b**. The process was always accompanied by a very significant decrease in molecular weight due to the favored β elimination produced by the presence of terminal 1-hexene inserted units.

In most cases the polydispersity is close to the typical value expected for "single site" catalysts, although occasional values higher than 3.0 are observed.

Experimental Section

General Considerations: All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glove box model HE-63. The solvents were pre-dried over sodium wire prior to purification by distillation under argon using the appropriate drying/deoxygenated agent: toluene, hexane and pentane (sodium-potassium alloy) and diethyl ether, THF (sodium-benzophenone). After being collected, the dried solvent was stored under argon in an ampoule over potassium mirrors or 4 Å molecular sieves (THF). Deuterated solvents from Scharlau were dried, degassed and stored over molecular sieves. C, H and N microanalyses were performed on a Perkin−Elmer 240B and/or Heraeus CHN−O-Rapid microanalyzer. IR spectra were performed in nujol mulls on a Perkin−Elmer 883 spectrophotometer. NMR spectra, measured at 25 °C, were recorded on a Varian Unity FT-300 (^{1}H NMR at 300 MHz, ^{13}C NMR at 75 MHz) or FT-500 (^{1}H NMR at 500 MHz, ^{13}C NMR at 125 MHz) spectrometer and chemical shifts were referenced to the residual protons or carbons of the deuterated solvents. MgMeCl and (2,6-xylyl)isocyanide were purchased

Table 3. Ethylene polymerization and ethylene/1-hexene copolymerization with **1a** and **1b**/MAO

Polymerization	Entry	μmol Zr	Al/Zr	% $C_{6\ M}$ [a]	g PE	Activity[b]	Polymer % C_6[c]	*M*w[d]	*M*w/*M*n
1a	1	5.0	1500	−	10.7	$2.14\cdot10^6$	−	95100	3.8
	2	5.0	1500	39	21.9	$4.38\cdot10^6$	6.69	22600	1.8
1b	3	0.8	10000	−	14.47	$1.81\cdot10^7$	−	284600	−
	4	0.4	10000	−	4.33	$1.08\cdot10^7$	−	−	3.1
	5	0.8	5000	−	4.57	$5.71\cdot10^6$	−	−	−
	6	5.0	1500	−	13.83	$8.33\cdot10^6$	−	289800	3.1
	7	0.4	10000	24	4.44	$1.11\cdot10^7$	2.22	154000	2.3
	8	0.4	10000	39	8.1	$2.03\cdot10^7$	3.64	101800	1.9
A[e]	9	0.8	10000	−	8.42	$1.05\cdot10^7$	−	270000	2.0
B[e]	10	0.8	10000	−	0.9	$1.06\cdot10^6$	−	35000	2.2

[a] % mol of comonomer. [b] g PE/mol Zr·h·bar. [c] % molar in the polymer. Determined by ^{13}C NMR.[d] Mw measured by GPC.[e] **A** Cp_2ZrCl_2. **B** $(Me_2SiCp_2)ZrCl_2$.

from Aldrich and used without further purification. [Zr{(η^5-2-$MeC_{13}H_8$)(η^5-C_5H_4)EMe_2}Cl_2] (E = C, Si)[26], Li(CH_2SiMe_3)[40] and K($CH_2C_6H_5$)[41] were prepared following the literature methods.

Preparation of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}Me_2] (2): A THF solution of ClMgMe (3.0 M, 0.5 mL, 1.52 mmol) was added to a stirred suspension of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}Cl_2] (**1b**) (0.35 g, 0.75 mmol) in diethyl ether (50 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for a further 12 h. The solvent was removed under reduced pressure and the mixture was extracted into hexane. The supernatant solution was then filtered through celite from the $MgCl_2$ residue, concentrated (10 mL) and cooled to -35 °C to give **2** as a pale yellow powder. Yield 0.27 g, 84%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = −1.29 (s, 3 H, ZrMe), 0.09 (s, 3 H, ZrMe), 0.41 (s, 3 H, SiMe), 0.53 (s, 3 H, SiMe), 1.95 (s, 3 H, CMe), 5.43 (m, 1 H, C_5H_4), 5.52 (m, 1 H, C_5H_4), 6.50 (m, 1 H, C_5H_4), 6.59 (m, 1 H, C_5H_4), 7.1−7.2 (m, 3 H, $C_{13}H_7$), 7.27 (m, 1 H, $C_{13}H_7$), 7.39 (m, 1 H, $C_{13}H_7$), 7.67 (m, 1 H, $C_{13}H_7$), 8.05 (m, 1 H, $C_{13}H_7$) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = −1.2 (SiMe), −0.8 (SiMe), 18.0 (CMe), 31.0 (ZrMe), 35.5 (ZrMe), 86.2 (C_{ipso}, Si*C*), 100.2 (C_{ipso}, Si*C*), 110.2, 113.0, 113.6, 120.3, 120.6, 122.1, 123.7, 125.4, 125.9, 127.3, 128.9; (CH, C_5H_4, $C_{13}H_7$), 128.5, 129.2, 131.2, 131.5, 131.7; (C_{ipso}, C_5H_4, $C_{13}H_7$) ppm. $C_{23}H_{26}SiZr$ (421.76): calcd. C 65.60, H 6.21; found C 65.81, H 6.28.

Preparation of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}($CH_2C_6H_5$)$_2$] (3): Diethyl ether (50 mL) at −78 °C was added to a mixture of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}Cl_2] (**1b**) (0.4 g, 0.86 mmol) and K($CH_2C_6H_5$) (0.22 g, 1.72 mmol) and the resulting suspension was allowed to warm to room temperature and stirred for a further 12 h. The supernatant solution was then filtered through celite from the KCl residue, concentrated under reduced pressure (10 mL) and cooled to -35 °C to give **3** as an orange solid. Recrystallization from toluene/hexane gave **3** as a microcrystalline solid. Yield 0.38 g, 78%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = −0.18 (d, 1 H, $ZrCH_2$, 11 Hz), 0.28 (d, 1 H, $ZrCH_2$, 11 Hz), 0.34 (s,3 H, SiMe), 0.46 (s, 3 H, SiMe), 1.75 (s, 3 H, CMe), 1.95 (d, 1 H, $ZrCH_2$, 11 Hz), 2.13 (d, 1 H, $ZrCH_2$, 11 Hz), 5.20 (m, 1 H, C_5H_4), 5.29 (m, 1 H, C_5H_4), 5.80 (m, 1 H, C_5H_4), 6.31 (m, 1 H, C_5H_4), 6.52 (m, 2 H, C_6H_5), 7.17−7.13 (m, 6 H, C_6H_5), 6.93 (s, 1 H, $C_{13}H_7$), 6.78 (m, 1 H, $C_{13}H_7$), 7.21(m, 1 H, $C_{13}H_7$), 7.22(m, 1 H, $C_{13}H_7$), 7.33(m, 2 H, C_6H_5), 7.41(m, 1 H, $C_{13}H_7$), 7.53(m, 1 H, $C_{13}H_7$), 7.89(m, 1 H, $C_{13}H_7$) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = −0.7 (SiMe), −1.3 (SiMe), 17.2 (CMe), 61.4 (CH_2), 68.4 (CH_2), 85.7 (C_{ipso}, Si*C*), 100.7 (C_{ipso}, Si*C*), 111.6, 113.6, 116.1, 121.1, 121.3, 122.5, 124.0, 124.0, 124.3, 125.3, 125.3, 126.3, 126.4, 126.4, 126.6, 127.6, 128.5, 128.7, 128.7, 128.9, 129.3; (CH.), 125.0, 128.8, 130.3, 131.0, 132.3, 153.4, 154.6 (C_{ipso}) ppm. $C_{35}H_{34}SiZr$ (573.95): calcd. C 73.24, H 5.97; found C 73.02, H 5.76.

Preparation of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}(CH_2SiMe_3)$_2$] (4): In a procedure analogous to that described above for **3** a mixture of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}Cl_2] (**1b**) (0.35 g, 0.75 mmol) and Li(CH_2SiMe_3) (0.14 g, 1.52 mmol) were reacted in diethyl ether (50 mL) to yield a pale yellow powder characterized as **4**. Yield 0.29 g, 68%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = −2.20 (d, 1 H, $ZrCH_2$, 11 Hz), −0.94 (d, 1 H, $ZrCH_2$, 11 Hz), −0.07 (d, 1 H, $ZrCH_2$, 11 Hz), −0.21 (s, 9 H, $SiMe_3$), 0.24 (s, 9 H, $SiMe_3$), 0.25 (d, 1 H, $ZrCH_2$, 11 Hz), 0.42 (s, 3 H, SiMe), 0.49 (s, 3 H, SiMe), 2.07 (s, 3 H, CMe), 5.58 (m, 1 H, C_5H_4), 5.66 (m, 1 H, C_5H_4), 6.68 (m, 1 H, C_5H_4), 6.79 (m, 1 H, C_5H_4), 7.15 (s, 1 H, $C_{13}H_7$), 7.17−7.4 (m, 5 H, $C_{13}H_7$), 7.60 (m, 1 H, $C_{13}H_7$), 8.07 (m, 1 H, $C_{13}H_7$) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = −1.5 (SiMe), −0.5 (SiMe), 2.6 ($SiMe_3$), 3.5 ($SiMe_3$), 18.3 (CMe), 47.7 (CH_2), 49.4 (CH_2), 88.4 (C_{ipso}, Si*C*), 103.8 (C_{ipso}, Si*C*), 111.8, 112.6, 112.9, 116.6, 119.7, 123.1, 123.8, 125.9, 126.2, 127.5, 128.9; (CH.), 125.3, 126.7, 130.4, 130.8, 132.2 (C_{ipso}) ppm. $C_{29}H_{42}Si_3Zr$ (566.12): calcd. C 61.53, H 7.48; found C 61.38, H 7.34.

Preparation of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}{Me}{η^5-C(Me)N(2,6-xylyl)}] (5): Diethyl ether (50 mL) was added to a mixture of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}Me_2] (**2**) (0.4 g, 0.95 mmol) and CN(2,6-xylyl) (0.12 g, 0.95 mmol) and the resulting suspension was stirred for a further 5 h. The solvent was completely removed under vacuum and the product was washed with cool pentane (10 mL) to give a pale yellow powder characterized as **5**. Yield 0.49 g, 89%. IR (Nujol): $\tilde{\nu}$ = 1585 ($\nu_{C=N}$) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = −1.20 (s, 3 H, ZrMe), 0.67 (s, 3 H, SiMe), 0.71 (s, 3 H, SiMe), 1.65 (s, 3 H, CMe), 1.94 (s, 3 H, CMe), 1.97 (s, 3 H, CMe), 2.36 (3 H, ZrCMe), 5.18 (m, 1 H, C_5H_4), 5.72 (m, 1 H, C_5H_4), 5.91 (m, 1 H, C_6H_3), 5.94 (m, 1 H, C_5H_4), 5.99 (m, 1 H, C_5H_4), 6.80 (m, 2 H, C_6H_3), 6.82 (s, 1 H, $C_{13}H_7$), 7.21 (m, 2 H, $C_{13}H_7$), 7.30(m, 1 H, $C_{13}H_7$), 7.45(m, 1 H, $C_{13}H_7$), 7.68(m, 1 H, $C_{13}H_7$), 7.74 (m, 1 H, $C_{13}H_7$) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = −0.9 (SiMe), −0.1 (SiMe), 19.2 (CMe), 19.4 (CMe), 19.6 (CMe), 22.2 (ZrCMe), 32.2 (ZrMe), 92.3 (C_{ipso}, Si*C*), 105.0(C_{ipso}, Si*C*), 106.2, 106.3, 106.4, 114.3, 118.6, 123.2, 123.7, 124.6, 125.0, 125.5, 126.2, 128.5, 128.9, 129.7 (*C*H, $C_{13}H_7$, C_6H_3), 119.8, 126.0, 127.8, 128.1, 129.4, 130.5, 132.6, 144.9; (C_{ipso}, $C_{13}H_7$, C_6H_3) 245.4 (*C*=N) ppm. $C_{34}H_{39}NSiZr$ (580.99): calcd. C 70.29, N 2.41, N 6.77; found C 70.41, N 2.52, H 6.82.

Preparation of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}{$CH_2C_6H_5$}{η^5-C($CH_2C_6H_5$)N(2,6-xylyl)}] (6): In a procedure analogous to that described above for **5** a mixture of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}($CH_2C_6H_5$)$_2$] (**3**) (0.5 g, 0.87 mmol) and CN(2,6-xylyl) (0.11 g, 0.87 mmol) were reacted in diethyl ether (50 mL) to yield an orange powder characterized as **6**. Recrystallization from toluene/hexane gave **6** as a microcrystalline solid. Yield 0.56 g, 91%. IR (Nujol): $\tilde{\nu}$ = 1600 ($\nu_{C=N}$) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.27 (d, 1 H, $ZrCH_2$, 9 Hz), 0.56 (d, 1 H, $ZrCH_2$, 9 Hz), 0.54 (s, 3 H, SiMe), 0.67 (s, 9 H, $SiMe_3$), 1.32 (s, 3 H, CMe), 1.96 (s, 3 H, CMe), 2.29 (s, 3 H, CMe), 3.60 (d, 1 H, CCH_2, 9 Hz), 3.68 (d, 1 H, CCH_2, 9 Hz), 5.24 (m, 1 H, C_5H_4), 5.28 (m, 1 H, C_5H_4), 5.82 (m, 1 H, C_5H_4), 6.00 (m, 1 H, C_5H_4), 6.15 (m, 1 H, C_6H_n), 6.41 (m, 2 H, C_6H_n), 6.66 (m, 1 H, C_6H_n), 6.8−7.10 (m, 10 H, C_6H_n), 6.84 (s, 1 H, $C_{13}H_7$), 7.18 (m, 1 H, $C_{13}H_7$), 7.29 (m, 1 H, $C_{13}H_7$), 7.37 (m, 1 H, $C_{13}H_7$), 7.44 (m, 1 H, $C_{13}H_7$), 7.57 (m, 1 H, $C_{13}H_7$), 7.71 (m, 1 H, $C_{13}H_7$) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = −0.4 (SiMe), −0.8 (SiMe), 19.5 (CMe), 19.7 (CMe), 20.6 (CMe), 44.6 (CCH_2), 47.0 ($ZrCH_2$), 94.9 (C_{ipso}, Si*C*), 106.3(C_{ipso}, Si*C*), 106.8, 108.9, 109.3, 118.4, 118.8, 119.4, 123.1, 124.0, 125.4, 125.5, 125.5, 125.8, 125.8, 125.9, 126.9, 127.2, 127.2, 128.3, 128.6, 128.7, 128.7, 129.0, 130.1, 130.1; ($C_{13}H_7$, C_6H_n), 122.9, 124.9, 125.7, 129.2, 129.3, 131.4, 136.2, 145.2, 155.9; (C_i, $C_{13}H_7$, C_6H_n), 244.5 (*C*=N; *n* = 3, 5) ppm. $C_{44}H_{43}NSiZr$ (705.13): calcd. C 74.95, N 1.99, H 6.15; found C 75.22, N 2.05, H 6.28.

Preparation of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}{CH_2SiMe_3}{η^5-C(CH_2SiMe_3)N(2,6-xylyl)}] (7): In a procedure analogous to that described above for **5** a mixture of [Zr{(η^5-2-$MeC_{13}H_7$)(η^5-C_5H_4)$SiMe_2$}(CH_2SiMe_3)$_2$] (**4**) (0.35 g, 0.62 mmol) and CN(2,6-xylyl) (0.08 g, 0.62 mmol) were reacted in diethyl ether (50 mL) to yield an orange powder characterized as **7**. Recrystallization from toluene/hexane gave **7** as a microcrystalline solid. Yield 0.37 g, 87%. IR (Nujol): $\tilde{\nu}$ = 1590 ($\nu_{C=N}$) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = −2.97 (d, 1 H, $ZrCH_2$, 12 Hz), −1.86 (d, 1 H, $ZrCH_2$, 12 Hz), −0.12 (s, 9 H, $SiMe_3$), −0.01 (s, 9 H, $SiMe_3$), 0.68 (s, 3 H,

SiMe), 0.70 (s, 3 H, SiMe), 1.83 (s, 3 H, CMe), 1.90 (s, 3 H, CMe), 2.45 (d, 1 H, CCH_2, 12 Hz), 2.57 (s, 3 H, CMe), 2.63 (d, 1 H, CCH_2, 12 Hz), 5.55 (m, 1 H, C_6H_3), 6.07 (m, 1 H, C_5H_4), 6.19 (m, 1 H, C_5H_4), 6.21 (m, 1 H, C_5H_4), 6.66 (m, 1 H, C_5H_4), 6.79 (m, 3 H, $C_{13}H_7$), 7.29 (m, 3 H, $C_{13}H_7$, C_6H_3), 7.47 (m, 1 H, $C_{13}H_7$), 7.67 (m, 2 H, $C_{13}H_7$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ = −0.43 (SiMe), −0.40 (SiMe), 0.9 ($SiMe_3$), 3.9 ($SiMe_3$), 19.6 (CMe), 20.4 (CMe), 20.6 (CMe), 22.7 (CCH_2), 32.3 ($ZrCH_2$), 96.5 (C_{ipso}, Si*C*), 106.2(C_{ipso}, Si*C*), 107.6, 107.7, 112.9, 115.6, 123.5, 124.2, 124.8, 125.3, 125.6, 127.8, 128.2, 128.5, 128.7, 128.8; ($C_{13}H_7$, C_6H_3), 124.6, 125.5, 129.6, 129.7, 130.6, 133.3, 134.8, 145.7; (C_i, $C_{13}H_7$, C_6H_3), 245.4 (*C*=N) ppm. $C_{38}H_{51}NSi_3Zr$ (697.30): calcd. C 65.45, N 2.01, H 7.37; found C 65.79, N 2.16, H 7.52.

X-ray Structure Determination for Complex 3: Orange crystals of compound **3** were obtained by cooling a concentrated toluene solution and a suitable sized crystal was mounted in a Lindemann tube and mounted on an Enraf−Nonius CAD 4 automatic four-circle diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073Å). Crystallographic and experimental details are summarized in Table 4. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by direct methods and refined by least-squares against F^2 (SHELXL 97).[42] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with the exception of the hydrogens of the CH_2 groups which were found in the difference Fourier map. The hydrogen atoms of the disorder toluene molecule were not included.

X-ray Structure Determination for Complex 6: Data were recorded using Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator and ω scans on a Nonius Kappa CCD diffractometer (see Table 4). The structure was refined anisotropically using the program SHELXL-97.[42] Hydrogen atoms were included using rigid methyl groups or a riding model.

CCDC-236220 (for **3**) and -236644 (for **6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Polymerization Procedures

Ethylene Polymerizations: Polymerizations were carried out in a Büchi autoclave equipped with a heating bath, mechanical stirrer and connection to argon-vacuum lines. The reactor was evacuated, flushed several times with argon and then charged at 25 °C with 600 mL of freshly distilled heptane and variable amounts of a 10% toluene solution of MAO. The solution was saturated and pressurized with ethylene at 4.0 bar and the thermostat set at 70 °C. Polymerization was started by injection of variable volumes of a previously prepared toluene solution of the zirconocene catalyst. The reaction was stopped by addition of 5 mL of acidified methanol (HCl/methanol, 1:1). Polymers were recovered by filtration, washed with methanol and dried under vacuum at 80 °C for 1 day. The molecular weight of the resulting polyethylene was evaluated by GPC.

Ethylene/1-Hexene Polymerizations: The same procedure described above was followed for copolymerization experiments, the appropriate volume of 1-hexene being initially charged into the reactor together with the solvent. The resulting copolymer was characterized by ^{13}C NMR spectroscopy in $C_6D_3Cl_3$ to evaluate the ethylene/1-hexene ratio by reported methods.[43]

Table 4. Summary of X-ray data for compounds **3** and **6**

	3	**6**
Empirical formula	$C_{35}H_{35}SiZr\cdot 1/2C_7H_8$	$C_{44}H_{43}NSiZr$
Color	orange	pale yellow
Molecular mass	621.40	705.10
Crystal habit	block	prism
a (Å)	9.611(2)	17.2139(10)
b (Å)	18.532(4)	12.1819(9)
c (Å)	17.891(4)	16.4343(10)
β (°)	104.63(3)	93.884(9)
V (Å^3)	3083.3(12)	3438.3(4)
Z	4	4
T (K)	293(2)	150(2)
$D_{calcd.}$ (g·cm^{-3})	1.336	1.362
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
F(000)	1292	1472
Crystal size (mm)	0.35 × 0.30 × 0.25	0.28 × 0.26 × 0.10
μ (mm^{-1})	0.421	0.388
2θ (max.)	52.02	54.96
Total/indep. reflns.	6357/5986	26898/7873
Limiting indices (*h*, *k*, *l*)	−11/0, 0/22, −21/22	−22/22, −15/15, −21/21
Data/restraints/parameters	5986/0/370	7873/381/429
R_{int}	0.0746	0.0501
Goodness of fit F^2	1.083	1.026
R int. [all data]	*R*1 = 0.1000, *wR*2 = 0.1649	*R*1 = 0.0585, *wR*2 = 0.0817
Final *R* int [$I > 2\sigma(I)$]	*R*1 = 0.0567, *wR*2 = 0.1463	*R*1 = 0.0344, *wR*2 = 0.0742
Largest diff. peak and hole [e·Å^{-3}]	0.723 and −1.179	0.312 and −0.494

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[1] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem. Int. Ed.* **1999**, *38*, 428−447.
[2] M. Bochmann, *J. Chem. Soc., Dalton Trans.* **1996**, 255−270.
[3] H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143−1170.
[4] H. G. Alt, A. Koppl, *Chem. Rev.* **2000**, *100*, 1205−1221.
[5] C. Janiak, in *Metallocenes, vol. 2* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, **1998**, pp. 547−614.
[6] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169−1203.
[7] K. C. Jayaratne, L. R. Sita, *J. Am. Chem. Soc.* **2000**, *122*, 958−959.
[8] E. Y. Tshuva, I. Goldberg, M. Kol, *J. Am. Chem. Soc.* **2000**, *122*, 10706−10707.
[9] I. M. Lee, W. J. Gauthier, J. M. Ball, B. Iyengar, S. Collins, *Organometallics* **1992**, *11*, 2115−2122.
[10] W. Roll, H. H. Brintzinger, B. Rieger, R. Zolk, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 279−280.
[11] W. Spaleck, F. Küber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E. F. Paulus, *Organometallics* **1994**, *13*, 954−963.
[12] U. Stehling, J. Diebold, R. Kirsten, W. Roll, H. H. Brintzinger, S. Jungling, R. Mülhaupt, F. Langhauser, *Organometallics* **1994**, *13*, 964−970.
[13] G. X. Xu, E. Ruckenstein, *Macromolecules* **1998**, *31*, 4724−4729.
[14] J. Imuta, Y. Toda, T. Matsugi, H. Kaneko, S. Matsuo, S. Kojoh, N. Kashiwa, *Chem. Lett.* **2003**, *32*, 656−657.
[15] J. Imuta, N. Kashiwa, Y. Toda, *J. Am. Chem. Soc.* **2002**, *124*, 1176−1177.
[16] D. R. Swanson, C. J. Rousset, E. Negishi, T. Takahashi, T. Seki, M. Saburi, Y. Uchida, *J. Org. Chem.* **1989**, *54*, 3521−3523.
[17] S. L. Buchwald, R. B. Nielsen, *Chem. Rev.* **1988**, *88*, 1047−1058.
[18] H. Yasuda, A. Nakamura, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 723−742.
[19] J. J. Alexander, *The Chemistry of the Metal-carbon Bond, vol. 2*, John Wiley & Sons, New York, **1985**.
[20] L. D. Durfee, I. P. Rothwell, *Chem. Rev.* **1988**, *88*, 1059−1079.
[21] A. M. Barriola, A. M. Cano, T. Cuenca, F. J. Fernández, P. Gómez-Sal, A. Manzanero, P. Royo, *J. Organomet. Chem.* **1997**, *542*, 247−253.
[22] E. L. Lyszak, J. P. O′Brien, D. A. Kort, S. K. Hendges, R. N. Redding, T. L. Bush, M. S. Hermen, K. B. Renkema, M. E. Silver, J. C. Huffman, *Organometallics* **1993**, *12*, 338−342.
[23] F. J. Berg, J. L. Petersen, *Organometallics* **1993**, *12*, 3890−3895.
[24] R. Fandos, A. Meetsma, J. H. Teuben, *Organometallics* **1991**, *10*, 2665−2671.
[25] M. Bühl, G. Hopp, W. vonPhilipsborn, S. Beck, M. H. Prosenc, U. Rief, H. H. Brintzinger, *Organometallics* **1996**, *15*, 778−785.
[26] A. Sebastián, P. Royo, P. Gómez-Sal, E. Herdtweck, *Inorg. Chim. Acta* **2003**, *350*, 511−519.
[27] M. F. Lappert, C. J. Pickett, P. I. Riley, P. I. W. Yarrow, *J. Chem. Soc., Dalton Trans.* **1981**, 805−813.
[28] M. F. Lappert, P. I. Riley, P. I. W. Yarrow, J. L. Atwood, W. E. Hunter, M. J. Zaworotko, *J. Chem. Soc., Dalton Trans.* **1981**, 814−821.
[29] A. Antiñolo, R. Fernández-Galán, B. Gallego, A. Otero, S. Prashar, A. M. Rodriguez, *Eur. J. Inorg. Chem.* **2003**, 2626−2632.
[30] R. Wolfgramm, C. Ramos, P. Royo, M. Lanfranchi, M. A. Pellingelli, A. Tiripicchio, *Inorg. Chim. Acta* **2003**, *347*, 114−122.
[31] H. R. H. Damrau, E. Royo, S. Obert, F. Schaper, A. Weeber, H. H. Brintzinger, *Organometallics* **2001**, *20*, 5258−5265.
[32] X. W. Zhang, Q. M. Zhu, I. A. Guzei, R. F. Jordan, *J. Am. Chem. Soc.* **2000**, *122*, 8093−8094.
[33] N. Schneider, F. Schaper, K. Schmidt, R. Kirsten, A. Geyer, H. H. Brintzinger, *Organometallics* **2000**, *19*, 3597−3604.
[34] A. Sebastián, P. Royo, O. Castaño, L. M. Frutos, C. Ramírez de Arellano, manuscript in preparation.
[35] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.
[36] R. Fandos, M. Lanfranchi, A. Otero, M. A. Pellinghelli, M. J. Ruiz, P. Terreros, *Organometallics* **1996**, *15*, 4725−4730.
[37] U. Segerer, S. Blaurock, J. Sieler, E. Hey-Hawkins, *J. Organomet. Chem.* **2000**, *608*, 21−26.
[38] H. H. Karsch, K. A. Schreiber, M. Reisky, *Organometallics* **1998**, *17*, 5052−5060.
[39] R. Kravchenko, R. M. Waymouth, *Macromolecules* **1998**, *31*, 1−6.
[40] M. Wedler, F. Knosel, F. T. Edelmann, U. Behrens, *Chem. Ber./Recueil* **1992**, *125*, 1313−1318.
[41] M. Westerhausen, W. Schwarz, *Z. Naturforsch., Teil B* **1998**, *53*, 625−627.
[42] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1998**.
[43] J. C. Randall, E. T. Hsieh, *ACS Symp Ser.* **1984**, *247*, 131−151.

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